J. Org. Chem. **1984**, *49*, 1653–1654

values diminish during the course of the reaction. These concentrations are too low for limiting conditions and thus the variation of selectivities from 1.8 to 8.5 with increasing bromine concentration which they report can be understood. They are the result of hydrogen abstractions with variable mixtures of S_σ, S_π, and Br chain carriers. It is noteworthy that even with the low concentrations of bromine they employed, with increasing bromine concentration, the BPI yields they report approach the value of zero we report at $[Br_2] > 10^{-2}$ M. There would have been agreement if their studies had been used to explore the trend of their data.

The choice of only method C, by Tanner and co-workers, for cyclopentane/cyclohexane in probing the properties of S_π was unfortunate since these secondary C–H systems operate efficiently with the Br· mediated chains. However, methods A and B can be used unambiguously on these systems for determining the selectivity with S_π since these "recipes" eliminate both Br· and S_σ as competitive hydrogen abstractors.

Experimental Section

All experiments are carried out as described earlier,[2-5,9] with repeated high vacuum degassing to eliminate oxygen. Photoinitiations were carried out with a medium-pressure mercury arc filtered through several layers of Pyrex. The volatile fraction, $C_6H_{11}Br$, C_5H_9Br, and $CHCl_3$ (detection limit 0.004 mmol) were analyzed by gas chromatography using an internal standard. BPI was recognized in the crude reaction mixture by its strong IR absorption at 2245 cm^{-1} and separated when present from the nonvolatiles by vacuum trap to trap distillation into a −10 °C trap, followed by ^1H NMR analysis with an internal standard.

Analysis of BPI. ^1H NMR ($CDCl_3$): δ 3.05 (t, 2 H, J = 3 Hz), 3.55 (t, 2 H, J = 3 Hz), detection limit (0.02 mmol). IR (CH_2Cl_2, cm^{-1}): most prominent band at 2245 (SNCO), 1735 (m), 1400 (m), 1070 (m), detection limit (0.006 mmol).

Acknowledgment. We thank the National Science Foundation for financial support of this work.

Registry No. Cyclopentane, 287-92-3; cyclohexane, 110-82-7; succinimidyl, 24344-83-0.

Reactions of Unsaturated Carbenes with Metal–Metal Bonds. Insertion Reactions with Se–Se and Te–Te Bonds

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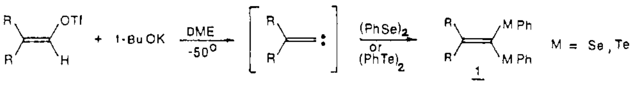
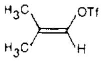
In recent years, the organic compounds of selenium and tellurium have proved to have an extremely rich chemistry. Their properties have aroused interest in many areas from synthesis[1] to use as electrical conductors.[2] Of particular interest are the compounds containing two heteroatoms bonded to the same carbon center, in which the substituent effects can greatly influence the reactivity of that site and may provide for a series of unique transformations about the carbon skeleton.[3]

However, little information is available in the case where two chalcogen groups are bound to an sp^2 hybridized carbon. Jensen and Henriksen reported the synthesis of such compounds in 1970 by the reaction of carbon diselenide with active methylene compounds.[4] Similar diselenides were prepared by Gröbel and Seebach via the Peterson olefination reaction.[5] No studies of possible synthetic utility of these compounds have been published to our knowledge, perhaps due to the lack of an easy high-yield preparation of these systems.

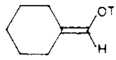
Scheme I



It occurred to us that our previous work with unsaturated carbenes[6] might provide a simple pathway to compounds of this type via the insertion reaction shown in Scheme I. Literature data showed that these metal–metal bonds were indeed reactive to insertion by saturated carbenes,[7] and while not truly analagous the sulfur–sulfur bond of disulfides had been reacted with both saturated[8] and unsaturated carbenes.[9] We therefore began a study of diphenyl diselenide and diphenyl ditelluride with triflates **2** and **3**.



2



3

In practice, the reactions proved to be easily performed and isolation and purification are quite straightforward. Reaction temperatures of −50 to −55 °C were maintained with a cold bath of bis(2-ethoxyethyl) ether and dry ice. Higher temperatures gave lower yields of product while lower temperatures led to solubility problems, especially with diphenyl ditelluride. No noticeable color change occurs during addition of *tert*-butoxide, and after changing solvent to hexane and filtering the precipitated salts, TLC shows only two major components present. These are easily isolated in pure form by column chromatography. The organic byproducts of the reaction come off the column well ahead of the highly colored band of excess trap. Since diphenyl diselenide and diphenyl ditelluride are fairly expensive, the recovery of highly pure unreacted starting material is an additional advantage in this method. The almost colorless carbene adduct follows soon after the last of the excess starting material, and this band is best monitored by TLC. Removal of the solvent at reduced pressure gives the products as viscous oils. Yields and spectral data are listed in Table I.

Spectra data matches well with expectations. The IR spectrum shows the monosubstituted phenyls, aliphatic C–H bands, and a weak carbon–carbon double bond in the area of 1730 cm^{-1}, which agrees well with the literature.[4] The mass spectra is very diagnostic due to the large number of isotopes of selenium and tellurium. In all cases, the calculated molecular ion isotope pattern matches extremely well with the experimental isotope pattern. The most abundant isotope of the pattern has been listed for each compound in Table I.

[†] Undergraduate Research Participant, University of Utah, Summer 1983.

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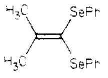
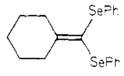
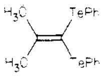
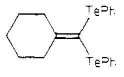
Table I. Spectral Properties and Yields of Products

compound	yield,[a] %	IR,[b] ν_{max}, cm^{-1}	^{1}H NMR,[c] δ (mult., H)	mass spectra,[d] %
 **4**	47	3050 (m), 2900 (s), 1725 (w), 1570 (s), 730 (s), 690 (s)	2.2 (s, 3), 7.1-7.3 (m, 5)	368 (18), 211 (22), 196 (21), 157 (34), 130 (100), 119 (100), 77 (42)
 **5**	61	3060 (m), 2920, 2860 (s), 1730 (w), 735 (s), 690 (s)	1.6 (m, 6), 2.75 (m, 4), 7.1-7.3 (m, 10)	406 (8), 251 (25), 169 (64), 141 (30), 115 (24), 91 (100), 77 (81)
 **6**	26	3060 (m), 2900 (m), 1740 (vw), 1670 (s), 740 (s), 700 (s)	2.3 (s, 3), 7.0-7.6 (m, 5)	466 (3), 261 (8), 207 (35), 129 (100), 77 (78)
 **7**	30	3060 (m), 2940, 2850 (s), 1730 (w), 1570 (s), 740 (s), 700 (s)	1.5 (m, 6), 2.6 (m, 4), 7.1-7.7 (m, 10)	504 (8), 410 (3), 301 (8), 207 (27), 170 (37), 77 (100)

[a] Isolated yields. [b] Neat. [c] $CDCl_3$, Me_4Si internal standard. [d] Most abundant isotope; 70 eV.

There is a marked difference in stabilities between the selenium and the tellurium products although both are isolable and easily handled. The selenium adduct is stable for weeks as an oil or in solution on the benchtop. Both tellurium products, however, decompose in solution to an insoluble white powder in a matter of days. The decomposition is much more rapid from chlorinated solvents (24 h) than with hexanes (~1 week). When left as a purified oil, decomposition of the tellurium compounds takes far longer. All four products, when stored as neat oils at 0 °C or less under argon, are stable for a month or more.

In summary, we have developed a new pathway for the synthesis of phenylseleno and phenyltelluro ketals. While yields of these compounds are moderate, the reaction is straightforward and purification simple. Studies of these compounds as to reactivities and possible synthetic applications are currently underway.

Experimental Section

Proton NMR spectra were recorded on a Varian EM-390 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer. Mass spectra were recorded on a VG Micromass 7070 double-focusing high-resolution mass spectrometer with VG Data System 2000.

Triflates were prepared by published procedures.[10,11] Diphenyl diselenide (Aldrich) and diphenyl ditelluride (Strem) were recrystallized from hexanes prior to use. DME was distilled from potassium/benzophenone directly into the reaction vessel. Hexanes were washed with concentrated H_2SO_4 and saturated $NaHCO_3$, dried over $MgSO_4$, and then distilled from CaH_2.

General Procedure for the Insertion of Alkylidenecarbenes into Se–Se and Te–Te Bonds. Reaction of Triflate 2 with Diphenyl Diselenide. To a flame-dried, three-necked, 250-mL round-bottomed flask equipped with argon inlet, addition funnel, and gas bubbler was added 100 mL of dry DME along with 1.5 g (4.8 mmol) of diphenyl diselenide and 0.6 g (2.9 mmol) of triflate **2**. The reaction mixture was cooled to −50 °C, and a solution of 0.4 g (3.6 mmol) of potassium *tert*-butoxide in 50 mL of dry DME was added dropwise via the addition funnel. After the addition, stirring was continued for 15 min at −50 °C; then the reaction was allowed to warm to room temperature. DME was then removed on a rotary evaporator and the residue taken up in hexanes and filtered. The resulting colored solution was chromatographed on activated silica gel by using hexanes as eluant. The product band is then stripped of solvent at reduced pressure to yield 0.5 g (47%) of diselenide **4** as a viscous yellow oil. Anal. Calcd for $C_{16}H_{16}Se_2$: C, 52.47; H, 4.41; Se, 43.12. Found: C, 52.99; H, 4.69; Se, 41.47.

Reaction of Triflate 3 with Diphenyl Diselenide. The reaction was performed according to the general procedure using 0.50 g (2.2 mmol) of triflate **3**, 1.5 g (4.8 mmol) of diphenyl diselenide, and 0.40 g (3.6 mmol) of potassium *tert*-butoxide. Isolated yield was 0.52 g (61%) of **5** as a yellow oil. Anal. Calcd for $C_{19}H_{20}Se_2$: C, 56.16; H, 4.97; Se, 38.87. Found: C, 56.23, H, 4.93, Se, 38.64.

Reaction of Triflate 2 with Diphenyl Ditelluride. The reaction was performed according to the general procedure using 0.20 g (0.98 mmol) of triflate **2**, 0.50 g (1.2 mmol) of diphenyl ditelluride, and 0.15 g (1.3 mmol) of potassium *tert*-butoxide. Isolated yield was 0.12 g (26%) of **6** as an orange oil.

Reaction of Triflate 3 with Diphenyl Ditelluride. The reaction was performed according to the general procedure using 0.25 g (1.1 mmol) of triflate **3**, 0.60 g (1.5 mmol) of diphenyl ditelluride, and 0.16 g (1.4 mmol) of potassium *tert*-butoxide. Isolated yield was 0.15 g (30%) of **7** as an orange oil.

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Registry No. **2**, 53282-30-7; **3**, 53282-32-9; **4**, 89438-15-3; **5**, 89438-16-4; **6**, 89438-17-5; **7**, 89438-18-6; diphenyl diselenide, 1666-13-3; diphenyl ditelluride, 32294-60-3.

A Mild Reductive Conversion of Oximes to Ketones

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A large number of ketone functional group equivalents are routinely employed in organic synthesis. Readily prepared and highly stable ketoximes (and oxime ethers) are useful in this regard both as protecting groups and selective activating groups. Notably, alkylation of dianions of oximes provides an excellent indirect method for highly regioselective monofunctionalization of ketones.[2] The utility of oximes as ketone equivalents is limited by methods employed for ketone regeneration. Thus, due to the relative hydrolytic stability of oximes,[3] a wide variety

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